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Summary of ORD Research Plan on the Leaching of Metals from Contaminated Solid Waste

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Background

The U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP) is the most common test used by regulatory agencies for classifying and comparing the leaching characteristics of different waste matrices. However, the test has several practical limitations and it simulates only one set of landfill disposal conditions. As a regulatory screening test, TCLP was not designed to account for several important parameters that significantly affect the kinetics of the reactions occurring at the solid-water interface including pH, reactant concentrations, reprecipitation reactions and secondary phase formations, physical characteristics of the solid wastes, residence time, and temperature. The need for more tailored and reliable assessment and prediction of leaching behavior of waste materials has evoked a need to incorporate these factors in evaluating the leaching behavior of waste materials generated anthropogenically or naturally.

Our main research goal is to develop consistent predictive methods, for short- and long-term risk assessment of waste materials containing environmentally toxic metals, which would integrate the contributions of critical geochemical factors in addition to pH. Using one but not all relevant parameters that can affect the dissolution and movement of toxic metals within the landfill can result in erroneous estimation of the long-term leaching potential of waste. Development and application of such predictive methods will aid in improving the current EPA approach of assessing metal leaching from anthropogenic and natural solid wastes.

Approach:

I. Critical review of current leaching tests and frameworks

- A critical review of past and recent advances in the area of waste leaching is currently underway.
- We are evaluating if any of leach testing and framework is applicable to wide variety of waste and disposal conditions.
- Evaluating methodology and whether it is adequate to simulate disposal conditions.
- Evaluating of current results and whether it is statistically valid. Are these leach tests and approach justified by the data and whether correlation with field data has been established?
- Can alternative conclusion be drawn from the results?

II. Leachate Data Collection

- Evaluating quality and quantity of leachate generated over time in several landfills in Ohio to determine the chemical stability of metals in active and closed landfills.
- Identify mobile metals and their chemistry
- Characterize leachate's chemical composition
- Utilize knowledge and data trends in bench-scale studies and future field validation studies.
- Determine whether leachate composition is at a steady-state
- Compare leachate composition with TCLP

III. Laboratory Studies

The main goal of the proposed research is to use macroscopic and spectroscopic analyses to develop consistent predictive methods, for short- and long-term risk assessment of waste materials containing environmentally important oxyanions (As, Cr, Se, and Mo), which would integrate the contributions of following geochemical factors such as leaching kinetics, pH, leaching agent, liquid/solid ratio, temperature, and aging of solid waste materials. Development and application of such predictive methods will aid in improving the current approach of EPA for accounting the toxicity of anthropogenic and natural solid wastes.

To achieve the research objective, the research plan has been divided into three main sections. The first section discusses the macroscopic experiments that will be conducted to assess the role of the geochemical factors of interest. The second section addresses the spectroscopic and microscopic studies for elucidation of the kinetic studies on molecular level. The third section deals with the development and testing of the predictive models that can accurately describe the leaching processes in natural environments.

1. Leaching Kinetics

Our research will study the desorption/dissolution kinetics of environmentally important metals such as As, Cr, Se, Mo, Pb, Cu, Cd and others under various reaction conditions relevant to the natural environments. Dissolution/ leaching kinetics depends on: (i) the liquid/solid interphase reaction kinetics; (ii) mass transfer effects; and (iii) the physicochemical properties of the solid particles. As a result the leaching kinetics will be studied as function of various combinations of the following parameters:

(a) pH and Eh

pH is one of the most important parameters that influences the speciation and solubility of inorganic constituents. Solubilities of most metal cations are strongly related to the solution equilibrium pH. Most oxides, hydroxides and carbonates are found in the positive Eh and alkaline pH ranges. Metal hydroxides may become soluble at higher pH (>12), in the absence of a strong reducing agent. Insoluble sulfides are found in slightly negative Eh and near neutral pH ranges. pH value of the rainwater ranges from 4.5 to 6.0. On the hand, the pH values of the leachant employed in the TCLP test are 2.9 and 4.9. Then again, the pH and Eh of the leaching agents in the real waste systems is a function of the geochemical conditions. Furthermore, sorption of metals to most adsorbents increases with increase in pH. This difference in pH and Eh can cause the higher than predicted concentrations of regulated metals in leachate. Thus, the current TCLP procedures may not truly represent the conditions existing in the landfills or waste repositories. Hence, there is a strong need to evaluate the leaching/dissolution kinetics as a function of pH and Eh.

(b) Solid/Liquid (L/S) ratio

The TCLP test employs a standard L/S ratio of 20:1. This ratio was chosen for analytical and administrative procedural purposes. However, the reactions at the solid/liquid interface are a function of the liquid/solid ratio. Subsequently, the overall leaching kinetics will also depend on this ratio. For example, if the 20:1 ratio is low then saturation will be experienced, which in turn may suppress the relative solubility of some constituents. Hence, the leaching kinetics of metals needs to be evaluated over wider L/S ratios than TCLP.

(c) Temperature

The nature of surface complex of a metal contaminant present in the solid waste directly impacts the mobility of that contaminant. Metals can sorb to hydrated metal oxides via inner-sphere (chemical sorption) or outer-sphere (physical sorption) complexation. The nature of a complexation can be best represented by its enthalpy, which can be evaluated from the change in reaction equilibrium with temperature. Temperature fluctuations in landfill, systems with seasonal variations, of over 40° are not uncommon. These changes in temperature can significantly change the nature of adsorption/ desorption mechanisms and thus the availability of the contaminants. Hence, the leaching kinetics of metals needs to be studied as a function of temperature range relevant to the natural environments.

(d) Aging

Current TCLP protocol requires that wastes be tested at the time of generation. The interaction of metals with the sorbents is also a function of their contact time. With time, the wastes may undergo physicochemical transformations, which in turn may discount the validity of TCLP results in predicting the leaching processes. Hence, the leach test, used for risk assessment purposes, should accommodate transformations that may be expected over the time frame of model predictions. To address this issue, the desorption/dissolution of the sorption complexes of metals needs to be evaluated with selected sorbents and their commonly occurring precipitates aged for different times

(e) Secondary Complexation reactions

In real wastes, other chemical species present may react with dissolved entities to form secondary precipitates. For example, cations such as Cu, Pb, or Fe present in the lumber-waste, may react with oxyanions of As to form metastable complexes. In another instance, in cement solidified/ stabilized wastes Ca species may complex with the oxyanions of As and Se to form insoluble precipitates. Then again, anions such as SO_4^{2-} and PO_4^{3-} may compete with Se oxyanions and enhance their leaching. Such secondary reactions may alter the overall as they significantly control the mobility of the metal contaminants in the ecosystems. Therefore, it is essential for a leaching-kinetics to account for the formation of such secondary precipitation reactions.

2. Microscopic and Spectroscopic Studies

To better understand the processes that control the mobility and bioavailability of metal contaminants a detailed characterization of the solid wastes is needed. In addition to the information on the particle size distribution, surface area, and chemical composition, chemical speciation and distribution must also be studied. Discernment of the chemical speciation is especially important for metal/ metalloids such as As, Cr, Fe, Mn, Mo, and Se that can exist simultaneously in multiple oxidation states.

3. Modeling

Based on the spectroscopic and microscopic revelations, the experimental results from the kinetics studies will be employed to develop and test the mathematical models to provide accurate mechanistic description of leaching behavior of both the simulated waste systems and the real solid wastes. The following structural properties of the solid waste will also be incorporated in the selected leaching model:

(a) Particle size distribution

The overall rate of a reaction is not only determined by the chemical equilibrium, but is also sensitive to the particle size. The particle size distributions in combination with the morphology control the reactive surface area of the solid reactants.

(b) Porosity and Pore Size Distribution

The overall leaching rate also is dependent on the porous nature of the solid waste particles. The greater the porosity the greater is the surface area available for the solid/liquid reactions. In dissolution reactions, the porosity of the solid phase will change with the reaction time, which in turn will influence the rate of reaction.

IV. Developing Suite of Tests Targeting Groups of Metals

There are many leaching tests in the literature aimed at evaluating the leaching behavior of materials under a variety of exposure conditions. They are used to obtain information about the characteristic properties of waste materials and on the short and long term leaching behavior of different constituents. Variables such as liquid/solid (L/S) ratios, leachant composition, pH, redox potential, complexation, ageing capacity and physical parameters are not addressed in some of these tests. Most of the tests are either a single batch tests, serial batch tests, pH controlled tests, or column tests. Each test is designed so as to address a certain aspect of leaching. A suite of leaching new and existing tests will be used to evaluate and to predict actual leachate composition from different types of waste. A series of extractions using a variety of leachants (acids, complexing agents, etc.) and several physical and chemical conditions will be used in modifying the leaching tests. Based on the waste characteristics and its disposal scenarios the user will choose the most suitable test based on the chemistry of metals in the waste.

V. Field Verification Studies

The objective of the work is to evaluate the validity of the suite of leaching tests and modeling as predictive tools for the evaluation of waste leaching form disposal sites. Leaching tests will be used to evaluate a range of contaminated waste and a clean reference waste. The reference waste will be placed in a place of cored samples in the field at a selected test location. Geologic drilling equipment and other sampling tools will be used to collect core samples from the waste mass and surrounding soil. Waste mass will be cored and tested in three locations: 1) the interior of the waste mass, 2) the perimeter of the waste to evaluate the interaction between the waste mass and adjacent subsoil, and 3) uncontaminated soil near the mass to evaluate the degree of leaching and transport as may be shown by spatial distribution of contaminants away from the monolith. At specified intervals during the duration of the study, the waste in the cored location will be retrieved and analyzed for using the suite of tests based on waste characterization and disposal conditions. Results from this field validation effort will play a major role in establishing how results from these validation tests should be interpreted and the role such tests should play in the regulatory decision-making process.